APPROXIMATE POLYNOMIAL EXPRESSIONS FOR RYDBERG – KLEIN – REES CURVES OF DIATOMIC COVALENT MOLECULES

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Abstract

A systematic method for fitting Rydberg – Klein – Rees (RKR) data with polynomial expressions is presented. The procedure is based on a change of variables that takes into account the form of the potential energy curve for large internuclear distances. The coefficients of the polynomial are determined by least squares. Results are presented for CO, HgH, and Ar_2. The form of the potential energy curves obtained is quite reasonable and the dissociation energies calculated are in satisfactory agreement with experimental data.

1.   Introduction

Within the context of the Born – Oppenheimer approximation [1,2], the potential energy for the motion of the nuclei is given by a function $U(R)$, of the nuclei coordinate vector R. As is well known, the function $U(R)$ is given as the sum

$$U(R) = V_{NN} + V(R), \tag{1}$$

where V_{NN} is the nuclear-nuclear repulsion energy and $V(R)$ the electronic energy function, which is the eigenvalue of the so-called electronic Hamiltonian. Knowledge of the function $U(R)$ is of utmost importance for the qualitative and quantitative

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understanding of molecular phenomena. The function $U(R)$ (vibrational potential) can be obtained by solving systematically the eigenvalue equation for the electronic Hamiltonian for a whole set of values of R [2]. However, the procedure requires a great deal of computation, and the results may depend on the particular algorithm used.

Alternatively, $U(R)$ may be constructed from spectroscopic data. Several methods have been proposed to this end (see, for example, refs. [3–7]), but the most exact one seems to be that developed by Rydberg, Klein and Rees (RKR) [8–10]. This procedure is particularly simple in the case of diatomic molecules, whose vibrational potential is completely specified by a single parameter R. From now on, we shall restrict ourselves to this case.

The RKR method allows one to compute the classical turning points from the knowledge of spectroscopic data (the rotovibrational energies). In the case of diatomic molecules, the technique can be formulated easily following the approach discussed in refs. [9] and [11], which makes use of the semiclassical quantization rule (JWKB approximation up to the first order [12]). Once the turning points for each vibrational energy level are obtained, one knows only a small part of the potential energy curve. The task that one now faces is to reconstruct the function $U(R)$ from these results.

A great deal of attention has been devoted to the construction of analytical expressions for the interatomic potential $U(R)$, based on spectroscopic data, since Dunham [13] first proposed the power series representation

$$U(R) = a_0 \lambda^2 (1 + a_1 \lambda + a_2 \lambda^2 + \dots); \quad \lambda = (R - R_e)/R_e . \tag{2}$$

Equation (2) is a reasonable approximation near the equilibrium distance R_e. However, it does not converge beyond $R = 2R_e$ because the potential $U(R)$ is singular at $R = 0$. Actually, its range of usefulness is quite smaller because the so-called Dunham coefficients a_i are not always very reliable or easy to compute up to a large order, even when a large number of turning points are known.

Several methods summarized by the expression

$$U(R) = c_0 f(\lambda)^2 \{1 + c_1 f(\lambda) + c_2 f(\lambda)^2 + \dots\} , \tag{3}$$

have been proposed to overcome these limitations [14–16], and they have been briefly reviewed elsewhere [4–7]. Different changes of variable $\lambda \to f(\lambda)$ are available to improve, to a certain extent, the convergence properties of the Dunham series. Padé approximants, built from eq. (2), have also been studied [17]. Although each of the above procedures presents some advantages, none is completely satisfactory. In particular, they fail to reproduce the correct asymptotic behavior of $U(R)$ for large internuclear separations. In order to derive better representations for the potential, it would be important to incorporate in an efficient way the information available for both the equilibrium and the infinite separation regimes.

In this paper, we suggest a new procedure to combine the RKR points with theoretical information about the behavior at infinite separation, in order to build analytically the whole potential energy curve. The essential feature of this method is a combination of least-squares fitting with techniques of analytical continuation of series expansions. We apply it for covalent diatomic molecules because the results obtained for this case are usually less accurate, a fact that makes them a good test for the method. Furthermore, a larger number of values of turning points are known for covalent molecules than for ionic compounds. The procedure is outlined in sect. 2, and applied to some covalent diatomic molecules in sect. 3. Further comments are found in sect. 4.

2. The method

Let R_e be the internuclear distance at the minimum of $U(R)$. The function

$$F(\lambda) = \lambda^{-2} U(R),\qquad(4)$$

where $\lambda = (R - R_e)/R_e$, is supposed to obey expansions of the form:

$$F(\lambda) = \sum_{i=0}^{\infty} F_i \lambda^i \,,\qquad(5a)$$

$$F(\lambda) = \lambda^a \sum_{i=0}^{\infty} f_i \lambda^{bi}, \quad b < 0,\qquad(5b)$$

about $\lambda = 0$ and $1/\lambda = 0$, respectively. The real numbers a and b define the large-R behavior. In the case of using the Dunham series (cf. eq. (2)), we have $F_i = a_i a_0$, $i = 1, 2, \ldots$, and $F_0 = a_0$.

The basis of our approach is the transformation

$$\lambda = w K^{1/b} (1 - w)^{1/b} \,,\qquad(6)$$

that maps $0 \leqslant \lambda < \infty$ onto $0 \leqslant w \leqslant 1$. Here, K is a real, positive parameter that allows us to control the transformation in order to generate a sequence of polynomials that approaches $F(\lambda)$. The function

$$S(K, w) = K^{-a/b} (1 - w)^{-a/b} F(\lambda(w)),\qquad(7)$$

remains infinite for all λ values, and in particular:

$$S(K, w \to 1) = \lim_{\lambda \to \infty} \lambda^{-a} F(\lambda) = f_0 \,.\qquad(8)$$

It can easily be shown that the Taylor expansion of $S(K, w)$ in power series of w, about $w = 0$,

$$S(K, w) = \sum_{n=0}^{\infty} \sigma_n(K) w^n, \tag{9}$$

has coefficients σ_n given by:

$$\sigma_n(K) = \sum_{i=0}^{n} (-1)^{n-i} \binom{(i-a)/b}{n-i} F_i K^{(i-a)/b}, \tag{10}$$

where $\binom{c}{i} = c(c - 1)(c - 2) \ldots (c - i + 1)/i!$ is the usual binomial coefficient. By contruction (cf. eqs. (6) and (7)), the function $S(K, w)$ possesses the correct basic analytic behavior expected for the exact function $F(\lambda)$. Furthermore, the bounded character of the variable w guarantees, at least, slowing the divergence of the original series in powers of λ. These two important properties allow us to provide an accurate representation of the unknown function of interest, $F(\lambda)$, from the knowledge of a number of Taylor coefficients F_i [7,8,18,19]. In this paper, we explore another possibility that is better suited to the problem posed, by use of the results provided by the RKR method. Nevertheless, in any case this analytical representation is qualitatively correct over the whole range of values of λ.

It is assumed that the sequence of partial sums

$$S_N(K, w) = \sum_{n=0}^{N} \sigma_n(K) w^n \tag{11}$$

converges towards $S(K, w)$ as N tends to infinity. Suppose now that we do not have a set of Taylor coefficients F_i as input information, but that a set of pairs of values $(\lambda_i, F(\lambda_i))$, $i = 1, 2, \ldots, 2M$ is available instead. For example, these $2M$ points may represent M pairs of left and right classical turning points. In this case, we can make use of the polynomials $S_N(K, w)$ to fit this set of points:

$$G_i = (w_i/\lambda_i)^a F(\lambda_i), \quad i = 1, 2, \ldots, 2M, \tag{12}$$

and to choose the coefficients $\sigma_i(K)$ so that

$$J_N^2 = (1/2M) \sum_{i=0}^{2M} [G_i - S_N(K, w_i)]^2, \tag{13}$$

is as small as possible. This is equivalent to a least-squares evaluation of $S_N(K, w)$. As J_N depends on K, it is not uniquely determined by eq. (13). Accordingly, we need an

appropriate criterion to choose an optimum value for K. In our case, we search K in such a way that

$$J_N^\star = J_N(K^\star) = \min_{\{K\}} J_N(K), \tag{14}$$

and evaluate $F(\lambda)$ by means of the sequence $S_N(K^\star, w)$. The optimum values of $\sigma_n(K)$, K, and the minimum of J will be denoted by $\sigma_n^\star$, $K^\star$, and $J^\star$, respectively.

The behavior of the potential energy function $U(R)$, for diatomic covalent molecules, at large internuclear distances has been the subject of numerous studies (see, for example, [20] and [21], and refs. quoted therein). The leading term depends on the nature of the atoms forming the molecule (open- or closed-shell atoms). In order to illustrate briefly our procedure, we consider here only the contribution due to van der Waals forces between atoms. That is, the potential energy should satisfy an expression of the type:

$$U(R) = D + C/R^6 + \ldots \ . \tag{15}$$

Since from eq. (4) we have for the function $F(\lambda)$

$$F(\lambda) = \lambda^{-2}(D' + C''/\lambda^6 + \ldots), \tag{16}$$

we may choose the exponents a and b in eq. (5b) as follows: $a = -2$ and $b = -6$. We notice that eq. (15) is not an expansion in power series of R^{-6}. Furthermore, as mentioned, some terms may be omitted (for instance, the one due to the polarization of an atom in the field of the other). Nevertheless, we shall adopt these two values for a and b because they correctly give us at least the two leading terms in the behavior of $U(R)$ for very large R for a number of molecules. Other cases can be treated by simply choosing a different value of b.

3.   Results and discussion

The electronic ground state of the CO molecule is one of the most studied ones. We use the RKR points and the value $R_e = 1.128341$ Å reported by Mantz et al. [22]. The $K^\star$ values found for $N = 5$ to 8 are shown in table 1, together with the calculated values for the dissociation energy, computed as:

$$D_N = S_N(K, 1). \tag{17}$$

The agreement with the experimental result can be considered as remarkable, taking into account that the RKR points fitted do not lie near the top of the well (that is, they do not depart too much from the equilibrium interatomic distance). Therefore,

Table 1

Minimum of the functional J_N, predicted dissociation energies, and percent deviations for a series of molecules. $[\delta_N = 100\,(1 - D_N/D_{exp})]$

Molecule	N	$K^{\star}$	$J_N^{\star}(K^{\star})$	D_N (cm^{-1})	δ_N
CO	5	43	29.16	74773.5	17.42
	6	60	4.85	75362.4	16.77
	7	45	4.46	76720.3	15.27
	8	67	2.51	75902.5	16.17
HgH	6	7800	1.75	3218.0	13.06
	7	4500	1.26	3300.9	10.82
	8	5000	1.08	3321.9	10.25
	9	7500	0.53	3299.4	10.86
Ar$_2$	6	300 000	6.64	76.8	23.21
	7	300 000	6.62	77.0	22.96
	8	300 000	6.39	77.8	22.16
	9	300 000	5.43	79.2	20.75
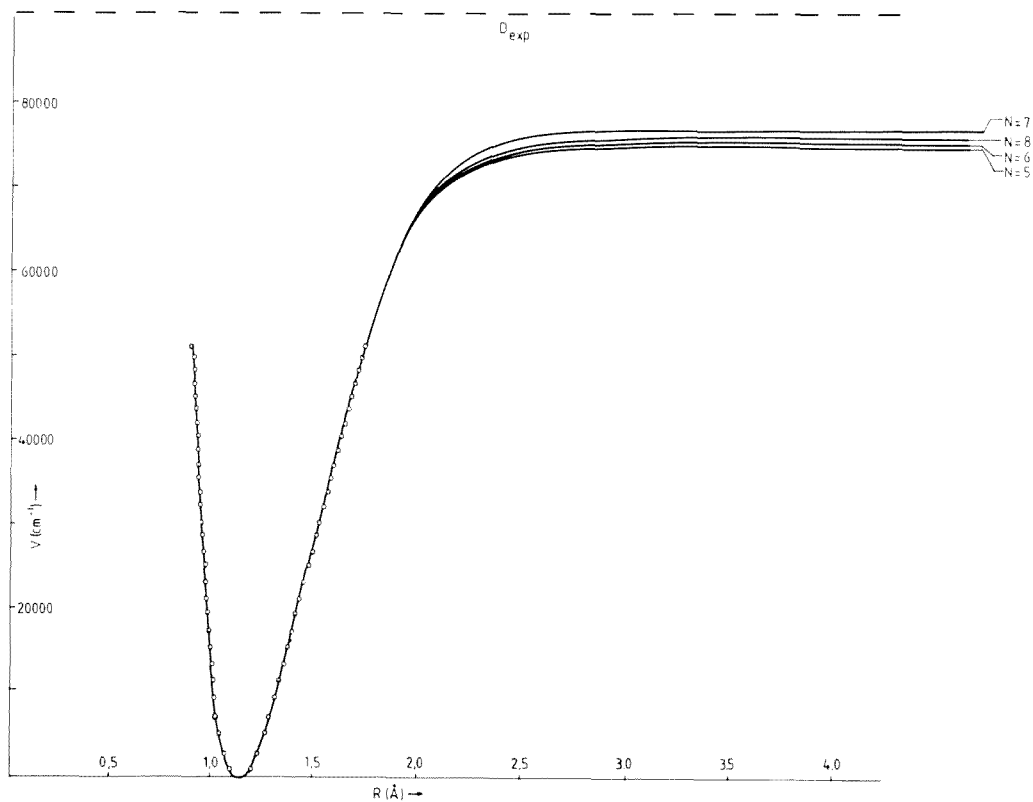
Fig. 1. Potential energy curve $U(R)$ for the CO molecule.

we conclude that the change of variables (6) takes properly into account the form of the function $U(R)$ at large internuclear distances. The potential energy curves obtained have been drawn in fig. 1.
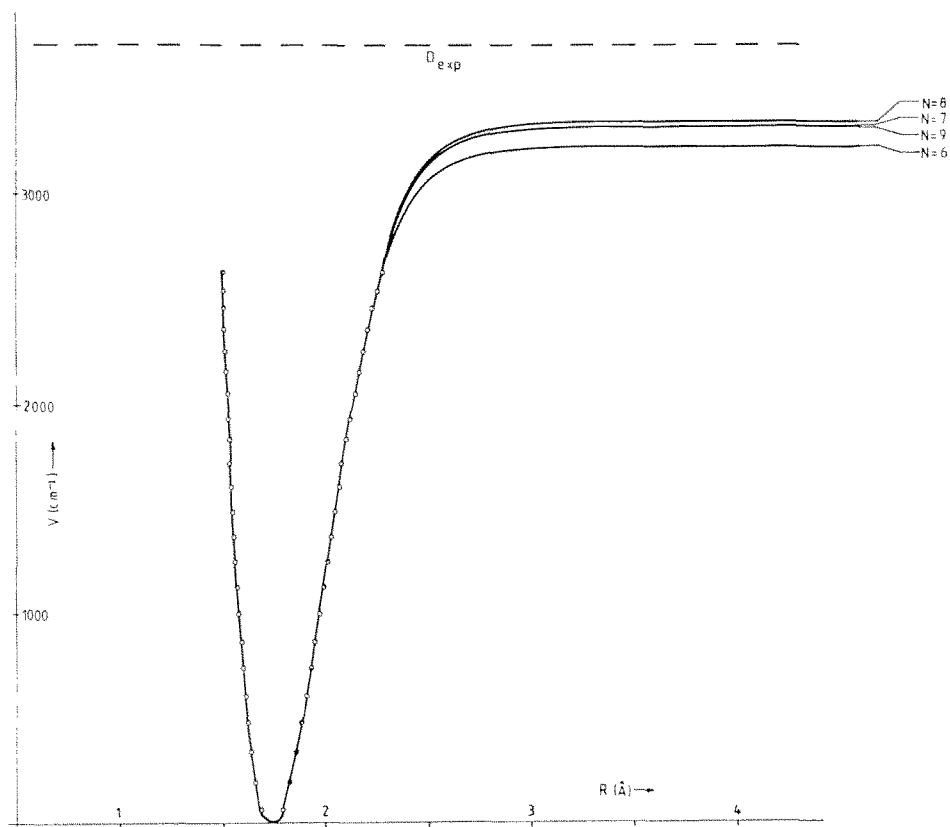

Fig. 2. Potential energy curve $U(R)$ for the HgH molecule.

As a second example, we used the RKR points for the HgH molecule, calculated by Stwalley [3], to fit an analytical potential for this molecule, using his value of R_e = 1.73469 Å. Table 1 and fig. 2 display the results obtained. The values of $J_N^\star$ obtained for this molecule are smaller than those in the previous example, and the $K^\star$ values are much larger.

Colbourn and Douglas [23] constructed an RKR function, that we use together with their value of R_e = 3.759 Å to perform a new example. Results are given in table 1 and fig. 3. Both the fitting of the potential energy curve and the agreement with the experimental dissociation energy are in this case poorer than in the previous two examples, because a smaller number of RKR points is available and they are less accurate. Comparing the $K^\star$ values for the three molecules in table 1, we conclude that the weaker the covalent bond, the larger the $K^\star$ values.
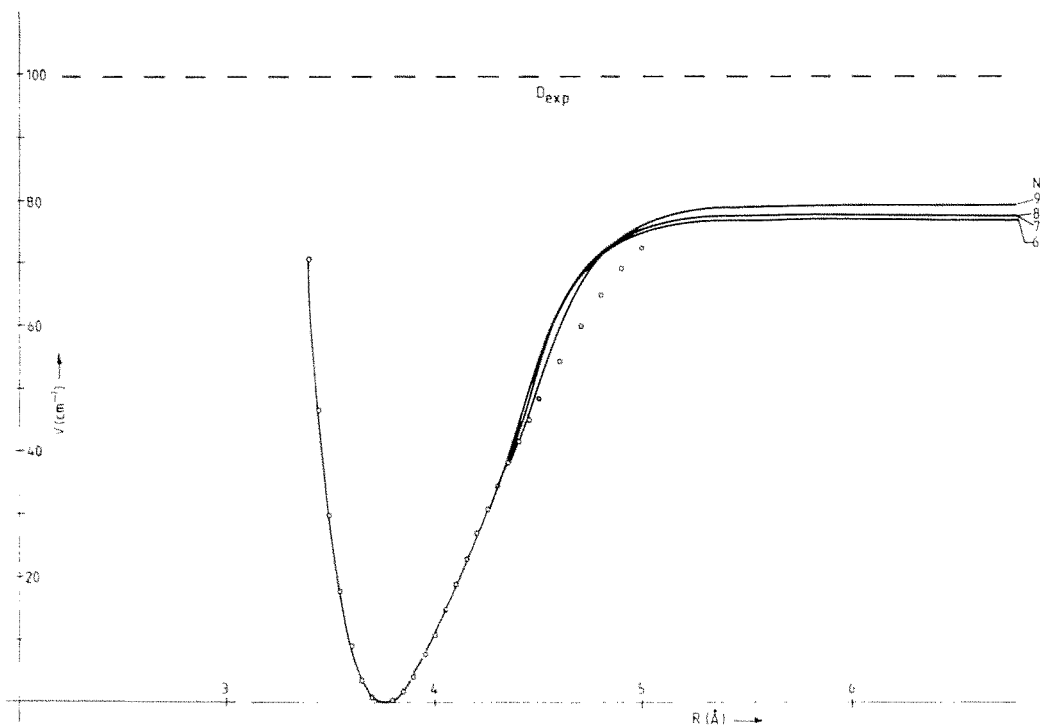
Fig. 3. Potential energy curve $U(R)$ for the Ar_2 molecule.

4.   Further comments

Here, it is worthwhile to make a comparison of our results for the dissociation energies with those obtained by other authors (see also ref. [6] for a discussion). As a most studied example, we choose the CO molecule. Only Thakkar's method [15] seems to be numerically better than ours, since it gives a deviation of $\delta \approx -3.6\%$ (against our result of 23.0%). However, his series is defective in that it has an unphysical maximum at $R \approx 5R_e$, as pointed out by Engelke [4]. This problem is shared by the Simons–Parr–Finlan series [12], which for $N = 4$ shows a distinct maximum at $R \approx 2.4\,R_e$ (and the potential function gives an exaggerate deviation of $\delta \approx 229\%$ for the dissociation energy). Another method in the literature (ref. [17]) also largely overestimates the results, leading to a deviation of $\delta \approx 182\%$ for the CO. There is also some evidence that the results obtained with these methods (refs. [15–17]) are not stable along sequences of increasing values of N (see ref. [6]).

We notice that the results are less accurate when the dissociation energy is very small (i.e. for the less deep potential wells). Nonetheless, no better results are available, as far as we know, for the case of van der Waals molecules (such as Ar_2) from the use of the RKR turning points.

Figures 1–3 show that the shape of the fitted potential energy curve does not substantially change as the number of terms in the polynomial $S_N(K, w)$ increases. This fact suggests that our systematic procedure is quite stable. This is an important advantage over other methods [15–17] which, as mentioned, show rather large variations in the predicted dissociation energies for varying N.

It should be kept in mind that the technique developed in the present paper is not restricted to the fitting of RKR points, and that the experimental data from other sources can also be handled in a similar fashion. In addition, the method is most suitable in those cases where the large-R behavior of $U(R)$ is known beforehand, since it can be accurately taken into account by properly choosing the parameters a and b in eqs. (4) and (5).

It is worth mentioning here that this present technique can be applied even in the presence of potential double wells or in the case of systems with similar characteristics due to the occurrence of avoided crossings. These features are frequently found, especially at intermediate and long distances. In this case, the input information consists of the asymptotic behavior of the dissociating state (for example, an ionic one) and the turning points corresponding to the dominating state near the equilibrium geometry (for example, a covalent one). One may think, however, that the quality of the results for double wells will not be as good as for single wells, because of the difficulty in describing the position and height of the relative maximum.

Acknowledgements

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